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Agent	Hong-Gyun Kim
Inventor	Ik-Hyeon Kwon
	Su-Myeong Choi
	Yeong-Su Wang
	Seong-Ryong Kim
	Jae-Sik Choi
	Tae-Jeong Lee
	Seok-Jong Han
	Myeong-U Kim
Applicant	HY SUNG CORPORATION
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Title of Invention	A process for preparing a highly homogeneous cellulosesolution

Abstract

The invention relates to the manufacturing method of the cellulose solution homogenizing in the low temperature. And after the cellulose powder is dissolved in the liquid concentration N-methylmorpholine N-oxide (NMMO) with small amount, it is about the method for manufacturing with the cellulose solution supplying solution and cellulose powder to extruder and dissolves in extruder with mixing, and swelling and homogenizes in the low temperature.

This can supply the NMMO solution due to the effect dissolving a small amount of pulp in the liquid concentration NMMO and is the melting point of NMMO decreased in the relatively low temperature to extruder. Cellulosic fiber with a superior flexibility and intensity the cellulose analysis generated in moreover, extruder in the swelling dissolution process of the high temperature is suppressed, in addition it is possible for the wide process temperature range the cellulose powder and NMMO solution smoothly can be expanded in the moreover low temperature and it can prevent from film being generated to the instantaneously melting by NMMO of the high temperature in the cellulose powder surface and the cellulose solution which finally homogenizes in the low temperature can be manufactured can be provided due to the reason for illustrating as described above.

Representative Drawing(s)

Fig. 1

Keyword(s)

The highly homogeneous cellulose solution, cellulosic fiber, N-methylmorpholine N-oxide, kneader, extruder.

Description

※ Brief Explanation of the Drawing(s)

Figure 1 is a process schematic diagram manufacturing the cellulose solution homogenizing of the invention.

Figure 2 is an aging temperature variation progress drawing according to the cellulose concentration

※ Details of the Invention

■ Purpose of the Invention

▸ The Technical Field to which the Invention belongs and the Prior Art in that Field

The invention relates to the manufacturing method of the cellulose solution homogenizing in the low temperature. And after the cellulose powder is more specifically dissolved in the liquid concentration N-methylmorpholine N-oxide (it hereinafter says to be 'NMMO') with small amount, it is about the method for manufacturing with the cellulose solution supplying solution and cellulose powder to extruder and dissolves in extruder with mixing, and swelling and homogenizes in the low temperature.

It is NMMO that the cellulose is widely used among the solvent in which melting is doubtful as the general solvent due to the crystalline structure in which affinity with the other material is very high but which is made as the strong hydrogen bond of the molecular chain or interchain and destroying this structure and manufacturing solution.

The recovery rate of solvent compares to the other wet spinning over 99% and it is very high and the low concentration NMMO of the minimum amount is ejected among the process to outside but the toxicity of the NMMO itself is worse than and the manufacturing process of the cellulosic fiber using the NMMO solvent is very much used to the environment-friendly product manufacture process which non-polluted the cellulose with the point to holding to material of film is high manufactured is the process. And this kind of methods beginning with US Patent No.3,447,935 and the method for being many is proposed.

In US Patent No.4,142,913, (4,144,080), and (4,196,282) and (4,246,221), the method it extruded after decompressing and distillates the water from NMMO aqueous solution including the cellulose expanding the cellulose in the NMMO aqueous solution containing the moisture less than 50% and is swollen and manufacturing dope and for making fiber was proposed.

The material property degradation by the pyrolysis can be caused since the long time these methods is required from melting to the radiation.

Moreover, it became the factor there is much consumption of the used energy and raising the manufacturing cost.

There can be the disadvantage it proposes the method for removing the moisture and manufacturing the cellulose solution, and that the production efficiency is low to the apparatus be complicated and this method manufacture the cellulose solution of the high viscosity as the thin film evaporator in the PCT WO WO94/06530 A.

And US Patent No.4,221,574 suggested the method it expanded the cellulose sheet in 95℃ through 65 by using 3 class amine oxide of the liquid containing the moisture of 15 weight% through 5 as solvent and for immediately stirring and heats this and radiating.

This method could not obtain the cellulose solution which the film formed in the pulp sheet surface therefore homogenized.

And US Patent No.4,416,698 suggests the method for agitating NMMO and cellulose pulp of the solid which is not liquid in the extruding device and radiating. And since using two kinds of compound powder as the large amount, the non-solution part is increased in solution and the method has this method in the mass production with the big problem.

Moreover, in the PCT WO WO1997/47790 A, the method for the fibrinoid cellulose powder and temperature being 50 ~ 130℃ and the moisture content dissolving the high concentration NMMO aqueous solution which is 20 weight% through 5 in the twin screw extruder after mixing and radiating is instead of presented with the cellulose pulp sheet.

There is a problem that the property of fiber is degraded due to the non-solution part of the large amount which the disadvantage of raising the cost by increasing the replacement frequency of the filter for the non-solution part and purging in the radiation, has this method, remains in solution since manufacturing the cellulose solution homogenizing.

And in US Patent No.4,416,698 presenting the manufacturing method of the cellulose solution and PCT WO WO1997/47790 A, the method for manufacturing the cellulose solution in extruder after mixing, swelling, and the dissolution process was shown. But these methods had the disadvantage of enough dissolving the cellulose.

※ The Technical Challenges of the Invention

The invention is worked out in order to solve the problem as described above and disadvantage. Firstly the cellulose powder of 5 weight% through 0.01 is dissolved in the liquid concentration N-methylmorpholine N-oxide (NMMO) with small amount and the NMMO solution is manufactured. In that way the NMMO solution can be supplied in the temperature which relatively is low due to the effect dissolving a small amount of pulp in the liquid concentration NMMO and is the melting point of NMMO decreased to extruder. The cellulose powder and NMMO solution smoothly can be expanded in the temperature it is possible for the wide process temperature range, low and it can prevent from film being generated in the cellulose powder surface and the cellulose solution which finally homogenizes in the low temperature can be manufactured.

Moreover, the present invention is to provide the cellulosic fiber with a superior flexibility of the cellulose at the high temperature swelling dissolution process within extruder and NMMO and intensity the cellulose solution which is manufactured in the low temperature homogenizing is used generation is suppressed.

※ Structure & Operation of the Invention

The invention according to the above characterizes the thing including the step (A): step (B) which swelling and the homogenized cellulose solution are manufactured with swelling and the cellulose solution through the extruder in which screw is arranged in order to supply the NMMO solution and cellulose powder to extruder and it gives the dispersion, mixing, shear, kneading, melting and scalability knuckle in extruder manufactures the NMMO solution in which the cellulose is dissolved it dissolves the cellulose powder of 3 weight% through 0.01 in the liquid concentration N-methylmorpholine N-oxide (NMMO) with small amount.

Moreover, it is preferable that the separate water evaporation apparatus in (B) step is not adhered and the cellulose solution is consecutively manufactured.

Moreover, it is preferable that the outward appearance diameter of the cellulose powder injected in (A) or (B) step is 500㎛ or less.

Moreover, it is preferable that the final cellulose solution is the content of the total weight comparison cellulose it dissolves in the extruder of (B) step with mixing, and swelling is the concentration of 20 weight% through 3.

Moreover, it is preferable that the NMMO solution is the total weight comparison moisture content in (A) step is 15 weight% through 10.

Moreover, it is preferable that in the cellulose in (B) step, the liquid NMMO dissolved with small amount is maintained by the temperature of 40℃ or 90℃ and it is supplied.

Moreover, it is preferable that L / D of the barrel of 3 or 16 or screw the extruder which is used in (B) step in order to manufacture the NMMO solution and cellulose powder with swelling and homogenization solution uses the twin screw extruder is the range of 12 through 64.

Moreover, it is preferable that the twin screw extruder is maintained by 30℃ or 110℃ temperature and it is performed.

Moreover, it is preferable that the screw speed of rotation of the twin screw extruder practices to 100rpm through 1,200rpm.

Moreover, it mixes with the other polymer and the cellulose powder of (A) or (B) step can use.

Hereinafter, specifically the invention attached is illustrated.

Fig. 1 schematically shows the processing procedure manufacturing the cellulose solution homogenizing in the low temperature as the embodiment of the present invention.

By using the pulverizing device adhered to the knife bar, in cellulose powders (2a, 2b) used in fig. 1, the grain size were 500㎛ this edge. And preferably thing less than 300㎛ is good.

If the size of the powder exceeds 500 ㎛, it constants, it is not swollen in kneader or the extruder (4) with the dispersion.

As long as it is possible, firstly a small amount of cellulose powder (2a) made with 500㎛ this harrow is dissolved in the concentration liquid NMMO (1).

5 weight% through 0.01 becomes the content of the cellulose powder (2a) about the concentration liquid NMMO (1). More preferably, it becomes 3 weight% through 0.1.

Moreover, the concentration of antioxidant 0.005 ~ 0.5 weight% very melts about the final cellulose with the pulp.

At this time, in case the content of the cellulose powder (2a) is 0.01 weight% less than, the melting point of NMMO and swelling goes lower but it is unable to contribute. In case of exceeding 5 weight% the viscosity of the NMMO solution (3) rises and it supplies the extruder (4) but problem is generated.

In the meantime, in the invention, the NMMO solution in which concentration is 10~50 weight% is concentrated on the normal method and it becomes the concentration liquid NMMO (1) in which the moisture content is 15 weight% through 10. Concentrate the moisture content to 10% less than but the cost increases and this is disadvantageous in the economical efficiency. The solubility is decreased if the moisture content exceeds with 15%.

The NMMO solution (3) in which the cellulose powder (2a) is dissolved with small amount and the cellulose solution which consecutively supplies the cellulose powder (2b) to the extruder (4) maintained by 105℃ through 65 and dissolves in the extruder (4) with mixing, and swelling and homogenizes are manufactured.

It is preferable that the cellulose powder (2a) the extruder (4) can be supplied with the NMMO solution (3) dissolved with small amount to the gear pump or the screw feeder. And moreover, the cellulose powder (2b) injects into the extruder (4) to the screw feeder.

According to the mixing within the extruder (4), and the content of the cellulose powder (2a) among swelling and the dissolved cellulose solution is the degree of polymerization of the cellulose polymer, more preferably, 14 weight% through 7 becomes concentration about the liquid NMMO (1) with 20 weight% through 3.

At this time, the case that the cellulose powder (2a) content is 3 weight% less than is unable to have the property as fiber. And the solution which homogenizes up a tree cannot be obtained to dissolve to the liquid NMMO (1) if 20 weight% is exceeded.

Moreover, it is preferable that in the powdered cellulose and solid phase NMMO in the invention in (B) step, the extruder (4) which is used in order to be injected and manufacture with swelling and the homogenized cellulose solution the twin screw extruder is desirable. And L / D of the barrel of 3 or 16 or screw the twin screw extruder is the range of 64 through 12. Barrel is 3 less than or the time when the cellulose solution passes through barrel is less and the non-solution part of L / D of screw 12 U.S. is generated and barrel exceeds with 16 or if L / D of screw exceeds 64, the excessive stress works on screw and screw is transformed into in other words.

Moreover, in the invention, it mixes the other polymer or additive and cellulose powders (2a, 2b) of (A) or (B) step can use. There can be the viscosity intensifier, the titanium dioxide, the discretization silica, the carbon, the ammonium chloride etc as additive it has the polyvinyl alcohol, carboxylmethylcellulose, the polyethylene glycol etc as polymer.

Fig. 2 shows that the solidification temperature of NMMO is drastically reduced to 40℃ in 75℃ even if the solidification temperature variation transition road of NMMO according to the cellulose concentration, and the cellulose the small amount (about 0.01~5%) is dissolved.

In the invention, the relatively low temperature can supply the extruder (4) with the NMMO solution (3) due to the effect dissolving a small amount of pulp in the liquid NMMO (1) and is the melting point of the liquid NMMO (1) decreased. Due to this, , in addition it is possible for the wide process temperature range the cellulose powder (2b) and NMMO solution (3) smoothly can be expanded in the moreover low temperature and it can prevent from film being generated in the cellulose powder (2b) surface and the cellulose solution which finally homogenizes in the low temperature can be manufactured.

Hereinafter, more specifically, the invention was explained by the embodiment but the invention was not restricted with the following embodiment. And the evaluation method as follows and method of measurement were used in the embodiment.

(a) The homogeneity of the cellulose solution.

When making the sample exit and dissolving the cellulose powder in extruder about the monohydrate NMMO (1 hydrate NMMO) to the fixation condition, the particle which was not dissolved was evaluated the solubility evaluation of the cellulose powder manufactured in the invention as the polarization microscope. And the non-solution part number within the slide glass 5×5㎟ area in which sample was placed was reckoned.

(b)Weight average polymerization degree(DPw)

By using the Ubbelohde viscometer, the inherent viscosity [IV] of the cellulose dissolved measured to be made 0.5M cupriethylenediamine hydroxide solution according to the ASTM D539-51T in 25±0.01℃ in the density range of 0.6 g/dl through 0.1.

While externally inserting the boiling point according to concentration and saving, it is *** and the inherent viscosity finds the degree of polymerization this for the sake to the equation of Mark-Houwink.

[IV] = 0.98×10-2DPw0.9

(c) The manufactured property of the cellulose fiber was measured in the invention like next.

Dry strength:107℃, and the intensity after 2 hours drying(g/d)

Wet strength:the intensity which it measures after leaving as it is in 25℃, 65RH with 24 hour and performing conditioning(g/d)

Embodiment 1.

The weight average polymerization degree put 1000 persons the cellulose sheet into the pulverizing device in which 100 mesh filter was mounted and the cellulose powder in which diameter was 500㎛ or less was manufactured. The cellulose powder was dissolved in NMMO. At this time, the content of the cellulose dissolved among the NMMO solution so that in 1 weight%, and antioxidant, 0.070 weight% be about the final cellulose.

After injecting the NMMO solution in which the cellulose was dissolved with 1 weight% into the extruder (4) in which inside was maintained by the casting temperature 68℃ by 78℃ to the gear pump to 6900g / time speed, it injected to the screw feeder to 784g / time with extruder and the residence time in the extruder swelling section to 0.8 minutes and temperature rose to 60~80℃ and the cellulose powder enough expanded the cellulose powder in the NMMO solution, each block temperature was maintained in the lysis zone of extruder with 95℃ through 90. After screw being operated to 200rpm and completely dissolving, it ejected through nozzle.

The ejected concentration of the solution was 11.1 weight%. And it was the state that the unmelted cellulose particle was not contained and that homogenized and it was the cellulose degree of polymerization 915.

Embodiment 2.

The weight average polymerization degree put 1200 persons the cellulose sheet into the pulverizing device in which 100 mesh filter was mounted and the cellulose powder in which diameter was 500㎛ or less was manufactured. The cellulose powder was dissolved in NMMO. At this time, the content of the cellulose dissolved among the NMMO solution so that in antioxidant, 0.08% be so that 2 weight% be. After injecting the NMMO

solution in which the cellulose was dissolved with 2 weight% into the extruder in which inside was maintained by 78℃ to the gear pump to 6900g / time speed with the casting temperature 59℃, it injected to the screw feeder to 676g / time with extruder and as to the residence time, 1.1 minutes the elevated temperature section in the extruder swelling section to 40~70℃ and the cellulose powder enough expanded the cellulose powder in the NMMO solution, each block temperature was maintained in the lysis zone within extruder with 95℃ through 90. After screw being operated to 200rpm and dissolving, it ejected through nozzle.

The ejected concentration of the solution continued with 10.7 weight%. And it was the state that the unmelted cellulose particle was not contained and that homogenized. It was the ejected cellulose degree of polymerization at the solution 1030.

Embodiment 3.

It changed the temperature of the lysis zone within extruder into 100℃ and after making identical with the embodiment 2, the other method ejected through nozzle.

It was the cellulose degree of polymerization at the solution doing makeup and was ejected while the cellulose particle was not nearly discovered 1015.

Embodiment 4.

The weight average polymerization degree put 850 persons the cellulose sheet into the pulverizing device in which 100 mesh filter was mounted and the cellulose powder in which diameter was 500㎛ or less was manufactured. The cellulose powder was dissolved in NMMO. At this time, the content of the cellulose dissolved among the NMMO solution so that in 1.5 weight% antioxidant, 0.13% be.

For in 63℃ NMMO solution and the cellulose powder in which the cellulose was dissolved with 1.5 weight%, the final concentration of the cellulose solution injecting to the twin screw type extruder and was manufactured, 14.5 weight% were.

The swelling local temperature of the twin extruder was maintained with 45~75℃ and the block temperature of the lysis zone was maintained with 95℃. After screw being operated to 300rpm and dissolving, it radiated through nozzle.

It was the cellulose degree of polymerization at the solution doing makeup and was ejected while the cellulose particle was not nearly discovered 760.

Comparative Example 1.

In the weight average polymerization degree is the pulverizing device 1200 persons the cellulose, after the powder which diameter pulverized with 500㎛ this harrow being immediately injected into the twin screw extruder with the liquid NMMO (1 hydrate) of 89℃ and each block temperature being maintained with 95℃ and dissolving, screw was ejected in 250rpm and it radiated.

The non-solution part of 100 ㎛ through the when observing solution the concentration of solution was 11 weight % through polarization microscope the diameter 50 existed. And it was the cellulose degree of polymerization 973.

Comparative example 2.

The temperature of the lysis zone was changed into 110℃ and after making identical with the Comparative Example 1, the other condition ejected within extruder through nozzle.

Did makeup and the cellulose degree of polymerization of the solution which was the small amount but was ejected was the cellulose particle 820.

	Embodiment 1.	Embodiment 2.	Embodiment 3.	Embodiment 4.	Comparative Example 1.	Comparative example 2.
Non-solution part evaluation.1)	0-1	0-2	0-6	0-9	24-36	14-19
Dry strength (g/d)	6.2	7.3	5.9	5.5	5.4	4.3
Drying elastic modulus (g/d)	310	321	267	273	240	191
Wet strength (g/d)	5.6	6.4	5.1	4.7	4.2	3.6

1) The non-solution part number within 5×5㎟ area.

▣ Effects of the Invention

The invention comprises the step that firstly dissolves the cellulose powder of 3 weight% through 0.01 in the liquid concentration N-methylmorpholine N-oxide (NMMO) with small amount and manufactures with the NMMO solution. This can supply the NMMO solution due to the effect dissolving a small amount of pulp in the liquid concentration NMMO and is the melting point of NMMO decreased in the relatively low temperature to extruder. , in addition it is possible for the process temperature range which is broad due to the reason for illustrating as described above the cellulose powder and NMMO solution smoothly can be expanded in the moreover low temperature and it can prevent from film being generated to the instantaneously melting by NMMO of the high temperature in the cellulose powder surface and the cellulose solution which finally homogenizes in the low temperature can be manufactured.

Moreover, cellulosic fiber with a superior flexibility and intensity the cellulose analysis generated in extruder in the swelling dissolution process of the high temperature is suppressed can be provided.

Scope of Claims

Claim 1 :

(A) The manufacturing method of the cellulose solution comprising: extruder a step for being manufactured to swelling and the homogenized cellulose solution in the low temperature through the extruder in which screw is arranged it gives the dispersion, mixing, the shear, the kneading, melting and scalability knuckle in extruder it supplies the step: (B) NMMO solution dissolving the cellulose powder of 3 weight% through 0.01 in the liquid concentration N-methylmorpholine N-oxide (NMMO) with small amount and manufactured with the NMMO solution the cellulose is dissolved and cellulose powder.

Claim 2 :

The manufacturing method of the cellulose solution of claim 1, wherein the outward appearance diameter of the cellulose powder injected in (A) or (B) step is 500㎛ or less.

Claim 3 :

The manufacturing method of the cellulose solution of claim 1, wherein in the final cellulose solution it dissolves in the extruder of (B) step with mixing, and swelling, the content of the total weight comparison cellulose is the concentration of 20 weight% through 3.

Claim 4 :

The manufacturing method of the cellulose solution of claim 1, wherein the total weight comparison moisture content is 15 weight% through 10.

Claim 5 :

The manufacturing method of the cellulose solution of claims 1 through 3, wherein in (B) step, the liquid NMMO in which the cellulose is dissolved with small amount is maintained by the temperature of 40℃ or 90℃ and it is supplied.

Claim 6 :

The manufacturing method of the cellulose solution of claim 1, wherein the extruder which is used in (B) step in order to manufacture the NMMO solution and cellulose powder with swelling and homogenization solution uses the twin screw extruder and L / D of the barrel of 3 or 16 or screw is the range of 64 through 12.

Claim 7 :

The manufacturing method of the cellulose solution of claim 6, wherein the twin screw extruder is maintained by 30℃ or 110℃ temperature and it is performed and especially, the temperature of the swelling section is 30~80℃.

Claim 8 :

The manufacturing method of the cellulose solution of claim 1, wherein the cellulose powder of (A) or (B) step mixes with the other polymer and it uses.

Claim 9 :

The cellulose solution in which the method of claim 1 is manufactured with the method of claim 1, and the non-solution part number within the slide glass 5×5㎟ area is 10 less than in the polarization microscope.

Claim 10 :

The cellulose molded product which the cellulose solution of claim 9 is manufactured with the cellulose solution of claim 9.

Drawings

Fig. 1

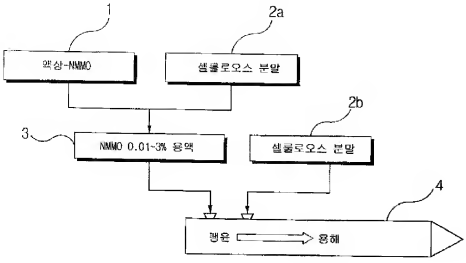

Fig. 2